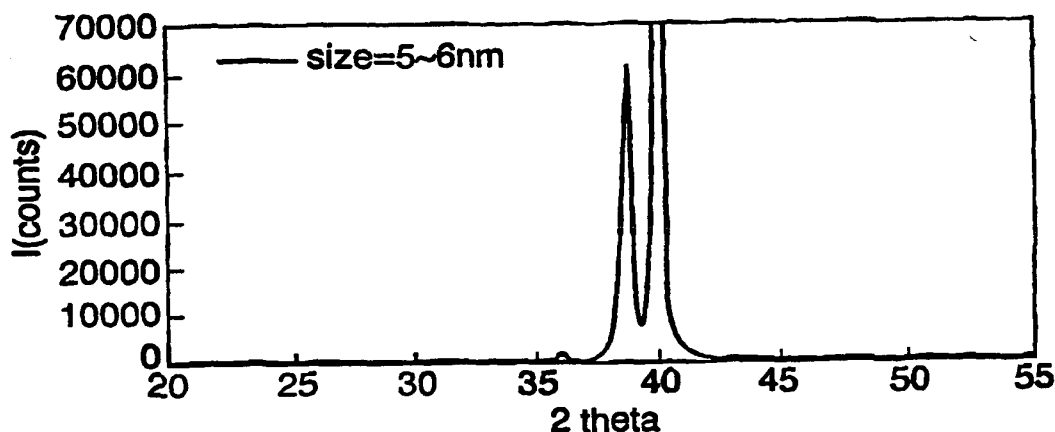




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

| | | | |
|---|--|--|--|
| (51) International Patent Classification: H01L 21/316, C23C 18/12 | | A1 | (11) International Publication Number: WO 00/65643 |
| | | | (43) International Publication Date: 2 November 2000 (02.11.00) |
| (21) International Application Number: PCT/GB00/01444 (22) International Filing Date: 14 April 2000 (14.04.00) (30) Priority Data: 9909375.9 24 April 1999 (24.04.99) GB (71) Applicant (for all designated States except US): THE SECRETARY OF STATE FOR DEFENCE [GB/GB]; Defence Evaluation & Research Agency, Ively Road, Farnborough, Hampshire GU14 0LX (GB). (72) Inventors; and (75) Inventors/Applicants (for US only): WHATMORE, Roger, William [GB/GB]; Cranfield University, SIMS, Bedford, Bedfordshire MK43 0AL (GB). ZHANG, Qi [GB/GB]; Cranfield University, SIMS, Bedford, Bedfordshire MK43 0AL (GB). HUANG, Zhaorong [GB/GB]; Cranfield University, SIMS, Bedford, Bedfordshire MK43 0AL (GB). (74) Agent: SEDGWICK, Freda; The Secretary of State for Defence, DERA Intellectual Property Department, A4 Bldg Room G016, Ively Road, Farnborough, Hampshire GU14 0LX (GB). | | (81) Designated States: JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report. | |

(54) Title: IMPROVEMENTS IN OR RELATING TO SOL GEL PROCESSING OF LEAD ZIRCONATE TITANATE THIN FILMS



(57) Abstract

A method of forming lead zirconate titanate thin films having a perovskite phase suitable for silicon signal processing circuitry by drying and firing one or more layers of a lead zirconate titanate precursor sol gel applied to a substrate at low temperatures (<500°C). The precursor is obtained by dissolving lead acetate in acetic acid, dehydrating and reacting the product with titanium isopropoxide and zirconium n-propoxide in methanol, optionally adjusting the concentration of the precursor to 0.4M using methanol, and adding ethylene glycol to the precursor in amounts sufficient to ensure the particle size in solution is less than 9 nanometers. Lead zirconate titanate thin films are produced by coating a substrate with one or more layers of the precursor sol gel, drying the or each layer at a temperature of about 200–300°C and firing one or more dried layers at a temperature of about 400–500°C.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

| | | | | | | | |
|----|--------------------------|----|--|----|--|----|--------------------------|
| AL | Albania | ES | Spain | LS | Lesotho | SI | Slovenia |
| AM | Armenia | FI | Finland | LT | Lithuania | SK | Slovakia |
| AT | Austria | FR | France | LU | Luxembourg | SN | Senegal |
| AU | Australia | GA | Gabon | LV | Latvia | SZ | Swaziland |
| AZ | Azerbaijan | GB | United Kingdom | MC | Monaco | TD | Chad |
| BA | Bosnia and Herzegovina | GE | Georgia | MD | Republic of Moldova | TG | Togo |
| BB | Barbados | GH | Ghana | MG | Madagascar | TJ | Tajikistan |
| BE | Belgium | GN | Guinea | MK | The former Yugoslav Republic of Macedonia | TM | Turkmenistan |
| BF | Burkina Faso | GR | Greece | ML | Mali | TR | Turkey |
| BG | Bulgaria | HU | Hungary | MN | Mongolia | TT | Trinidad and Tobago |
| BJ | Benin | IE | Ireland | MR | Mauritania | UA | Ukraine |
| BR | Brazil | IL | Israel | MW | Malawi | UG | Uganda |
| BY | Belarus | IS | Iceland | MX | Mexico | US | United States of America |
| CA | Canada | IT | Italy | NE | Niger | UZ | Uzbekistan |
| CF | Central African Republic | JP | Japan | NL | Netherlands | VN | Viet Nam |
| CG | Congo | KE | Kenya | NO | Norway | YU | Yugoslavia |
| CH | Switzerland | KG | Kyrgyzstan | NZ | New Zealand | ZW | Zimbabwe |
| CI | Côte d'Ivoire | KP | Democratic People's Republic of Korea | PL | Poland | | |
| CM | Cameroon | KR | Republic of Korea | PT | Portugal | | |
| CN | China | KZ | Kazakhstan | RO | Romania | | |
| CU | Cuba | LC | Saint Lucia | RU | Russian Federation | | |
| CZ | Czech Republic | LI | Liechtenstein | SD | Sudan | | |
| DE | Germany | LK | Sri Lanka | SE | Sweden | | |
| DK | Denmark | LR | Liberia | SG | Singapore | | |
| EE | Estonia | | | | | | |

Improvements in or relating to sol gel processing of lead zirconate titanate thin films

5 The present invention concerns improvements in or relating to the preparation and processing of thin films of lead zirconate titanate. More especially, but not exclusively, the invention concerns the preparation and processing of lead zirconate titanate thin films having a perovskite phase at low temperatures ($< 500^{\circ}\text{C}$) for the integration of the thin films with silicon signal processing circuitry.

10

Ferroelectric lead zirconate titanate ($\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$) (PZT) thin films are of growing technological interest for a diverse range of applications including nonvolatile semiconductor memory, optical modulator, high-frequency surface acoustic wave (SAW) devices, and pyroelectric infra-
15 red detectors.

PZT thin films which have been prepared at high temperatures ($> 500^{\circ}\text{C}$) exceed the limit of the temperature that the Al/Si metallisation on a silicon substrate such as a substrate for use in preparation of signal
20 process circuitry can stand.

The present invention aims to remedy this drawback. A desired object of the invention is the preparation of a PZT sol gel precursor and the formation from such precursor of PZT films, preferably having perovskite
25 orientation, at low temperatures ($< 500^{\circ}\text{C}$) by control of reaction conditions during the preparation of the PZT sol gel precursor in addition to the control of the coating conditions.

According to a first aspect of the invention there is provided a process for
30 preparing a lead zirconate titanate precursor sol comprising the steps of

dissolving lead acetate in acetic acid wherein the ratio of lead acetate to acetic acid is between 1g:1ml and 1g:3ml; dehydrating the mixture by distillation; reacting the lead acetate solution with a mixture of zirconium n-propoxide and titanium isopropoxide dissolved in methanol; optionally
5 adjusting the concentration of the precursor to 0.4M using methanol; and adding ethylene glycol to the precursor in amounts sufficient to ensure the particle size in solution in less than 9 nanometers.

The process uses lead acetate, titanium isopropoxide and zirconium n-propoxide as the basic precursors, which are dissolved in mixtures of
10 acetic acid and methanol, with ethylene glycol used as an additive. Preferably, the ratio of added ethylene glycol to lead is in the range 1:1 to 1:5 (wt%).

15 A key aspect of the process which has not been described before is the control of the particle size of the moieties suspended in the sol. This, coupled with precisely determined ratios of the chemicals, particularly the amounts of acetic acid and ethylene glycol used, allow us to obtain very low firing temperatures when producing lead zirconate titanate films using
20 the sol.

According to a second aspect of the present invention there is provided a process of coating a substrate with one or more layers of lead zirconate titanate having a substantially completely perovskite orientated phase
25 comprising the steps of applying a layer of the precursor according to the first aspect of the invention to the substrate, drying the layer at a temperature of 100-400°C and either a) firing the dried layer at a temperature of 400-500°C and applying further layers if required; or b) applying and drying one or more further layers before firing the dried

layers at a temperature of 400-500°C to anneal them together and applying further layers if required.

The advantages of such PZT films are that they show a pyroelectric effect. It will readily be appreciated by those skilled in the art that any material which shows a pyroelectric effect will also exhibit piezoelectric properties which mean that thin films of such materials can be used in electronic devices exploiting the effect, such as microphones, accelerometers, motors, actuators, and resonant devices for the filtering of radio frequency signals.

A number of specific but non-limiting examples of the process used will now be described in detail with reference to the figures in which

Figure 1 shows an XRD pattern of a ten layer film made using a coating solution prepared according to process 1 wherein each layer was dried at 200°C for 3 mins and annealed at 480°C for 15 min;

Figure 2 shows the relationship of (III) orientation of PZT perovskite phase to drying temperature;

Figure 3 shows the relationship of annealing temperature and time for the formation of perovskite PZT phase for a three layer film;

Figure 4 shows the XRD patterns of the PZT films made using sols of different particle size;

Figure 5 shows the XRD patterns of three PZT films of varying ratios of lead acetate to acetic acid;

Figure 6 shows the XRD patterns of two 12 layer PZT films annealed at 460°C and 480°C respectively with two layers fired together;

5

Figure 7 shows the electric properties of a 12 layer PZT film made from a coating solution of process 1 each layer dried at 200°C for 3 min and two layers annealed together at 460°C for 120 min;

10

Figure 8 shows the relationship of dc with time under a constant bias voltage of 20 volts of a PZT film made by method 2 from a coating solution of process 1; and

Figure 9 shows the I-V and Ry-V curves for a PZT film made by method 2 from a coating solution of process 1.

1. Manipulation of air sensitive solutions

Standard Schlenk technique was used during the manipulation of air sensitive solutions. Air sensitive solutions were stored under nitrogen in a dry box. The raw materials were transferred into reaction vessels using dry box techniques.

2. Sources and Purification of raw materials

Lead acetate $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (A.R. grade) was purchased from Fisher Scientific Chemicals, UK. It was calibrated and found to be 99.99% pure.

30

Titanium isopropoxide $\text{Ti}(\text{O}^i\text{Pr})_4$ (99.999%) was purchased from Aldrich. The $\text{Ti}(\text{O}^i\text{Pr})_4$ was further purified by distillation prior to use.

Zirconium n-propoxide $\text{Zr}(\text{O}^n\text{Pr})_4\text{Pr}^n\text{OH}$ (70 wt.%) was purchased from Aldrich. It was calibrated and found to vary in the range 70-78 wt.% but not further purified before use.

Methanol (anhydrous, 99.8%) was purchased from Aldrich and was not further dried before use.

10

3. Preparation of PZT Precursor Sols

Process 1:

15 Step 1a - Lead acetate $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (20g) was dissolved in acetic acid CH_3COOH (20ml) with gentle warming. Here the ratio of lead acetate to acetic acid is 1g:1ml. The colourless solution was heated to reflux at 116-117°C for 3h in air, then distilled to remove the water until the temperature of the vapour reached 105°C for 5 mins. 4~5ml of
20 distillates was collected. The solution was cooled to room temperature.

Step 2a - Zirconium n-propoxide $\text{Zr}(\text{O}^n\text{Pr})_4\text{Pr}^n\text{OH}$ (76%) (6.1g) was mixed with Titanium isopropoxide $\text{Ti}(\text{O}^i\text{Pr})_4$ (9.4g) in a glove box. The mixture containing the Zr and Ti precursors was stirred for 3 min. under
25 nitrogen. Methanol (20ml) was added to the Zr/Ti mixed solution. A white solid was formed straight away. The system was heated to reflux for 2.5h (white solid did not dissolve at this stage). The lead precursor of step 1a was added to the Zr/Ti mixed system in a dry environment (glove box). Then the new mixture was heated to reflux for 2h. All the solids
30 were dissolved in a few minutes after mixing. A yellow solution was

formed and filtered in air through a 0.2μ filter (ZapCap-CR filters, hydrophilic nylon membrane, Aldrich) after the solution had cooled to room temperature. The PZT precursor concentration was adjusted to 0.4M by adding methanol (70-80ml) in air. Ethylene glycol (5g) was added to the solution immediately. The solution was then stirred for 3 min at room temperature. The formed PZT solution was stored under nitrogen in a dry box or in the fridge (0°C) overnight prior to use. pH value of the solution is 4.0.

10 Process 2:

Step 1b - Lead acetate $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (20g) was dissolved in acetic acid CH_3COOH (40ml) with gentle warming. Here the ratio of lead acetate to acetic acid is 1g:2ml. The colourless solution was heated to reflux at $116-117^{\circ}\text{C}$ for 3h in air, then distilled to remove the water until the temperature of the vapour reached 105°C for 5 mins. 4~5ml of distillates was collected. The solution was cooled to room temperature.

Step 2b - Zirconium n-propoxide $\text{Zr}(\text{O}^n\text{Pr})_4 \cdot n\text{PrOH}$ (76%)(6.1g) was mixed with Titanium isopropoxide $\text{Ti}(\text{O}^i\text{Pr})_4$ (9.4g) in a glove box. The mixture containing the Zr and Ti precursors was stirred for 3 min. under nitrogen. Methanol (20ml) was added to the Zr/Ti mixed solution. A white solid was formed straight away. The system was heated to reflux for 2.5h (white solid did not dissolve at this stage). The lead precursor of step 1b was added to the Zr/Ti mixed system in a dry environment (glove box). Then the new mixture was heated to reflux for 2h. All the solids were dissolved a few minutes after mixing. A yellow solution was formed and filtered in air through a 0.2μ filter (ZapCap-CR filters, hydrophilic nylon membrane or teflon membrane, Aldrich) after the solution had cooled to room temperature. The PZT precursor was adjusted to 0.4M by adding

methanol (50 ~ 60ml) in air. Ethylene glycol (10g) was added to the solution immediately. The solution was then stirred for 3 min at room temperature. The formed PZT solution was stored under nitrogen in a dry box or in the fridge (0°C) overnight prior to use. pH value of the solution is 3.52.

Process 3:

Step 1c - Lead acetate $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$ (20g) was dissolved in acetic acid CH_3COOH (60ml) with gentle warming. Here the ratio of lead acetate to acetic acid is 1g:3ml. The colourless solution was heated to reflux at 116-117°C for 3h in air, then distilled to remove the water until the temperature of the vapour reached 105°C for 5 mins. 4 ~ 5ml of distillates was collected. The solution was cooled to room temperature.

15

Step 2c - Zirconium n-propoxide $\text{Zr}(\text{O}^n\text{Pr})_4 \cdot n\text{PrOH}$ (76%) (6.1g) was mixed with Titanium isopropoxide $\text{Ti}(\text{O}^i\text{Pr})_4$ (9.4g) in a glove box. The mixture containing the Zr and Ti precursors was stirred for 3 min. under nitrogen. Methanol (20ml) was added to the Zr/Ti mixed solution. A white solid was formed straight away. The system was heated to reflux for 2.5h (white solid did not dissolve at this stage). The lead precursor of step 1c was added to the Zr/Ti mixed system in a dry environment (glove box). Then the new mixture was heated to reflux for 2h. All the solids dissolved immediately. A yellow solution was formed and filtered in air through a 0.2µ filter (ZapCap-CR filters, hydrophilic nylon membrane or teflon membrane, Aldrich) after the solution had cooled to room temperature. The PZT precursor was adjusted to 0.4M by adding methanol (30 ~ 40ml) in air. Ethylene glycol (10g) was added to the solution immediately. The solution was then stirred for 3 min at room temperature. The formed PZT solution was stored under nitrogen in a dry

20

25

30

box or in the fridge (0°C) overnight prior to use. pH value of the solution is 3.29.

4. Coatings

5

Method 1

The concentration of coating solution made by any one of processes 1-3 was 0.4M. The substrate was Pt/Ti/SiO₂/Si (100nm/5nm/400nm/(100)).

10 Spin coating equipment was a photo resist spinner (Model 1-EC101D-R790), Headway Research Inc). Spin coating conditions were 3000rpm for 30 seconds at room temperature. Two hot plates were used to dry and decompose PZT films. One hot plate was set at 200°C and the other had higher temperature (CEE Custom Model 1100 Hotplate, Brewer Science,

15 Inc). Both hot plates were calibrated by a SensArray's Process Probe wafer (Intertrade Scientific). Coatings were put on the 200°C hot plate for 3 min for drying and then firing at higher temperature. The firing time depends on the temperature. At 460°C, it needs 60min and at 480°C, it needs 15 min for each layer. More layers can be built on by repeating

20 above procedure. A 1µm thick crack-free film needs 12~14 layers.

Method 2

Another way to make films is to anneal two layers together after each

25 layer was dried. The concentration of coating solution made by any one of processes 1-3 was 0.4M. The substrate was Pt/Ti/SiO₂/Si (100nm/5nm/400nm/(100)). Spin coating equipment was a photo resist spinner (Model 1-EC101D-R790, Headway Research Inc). Spin coating conditions were 3000rpm for 30 seconds at room temperature. Two hot

30 plates were used to dry and decompose PZT films. One hot plate was set

at 200°C and the other had higher temperature (CEE Custom Model 1100 Hotplate, Brewer Science, Inc). Both hot plates were calibrated by a SensArray's Process Probe wafer (Intertrade Scientific). Each layer was dried at 200°C and every two layers were annealed at higher temperatures.

- 5 The firing time depends on the temperature (see Results). More layers can be built on by repeating above procedure. A 1µm thick crack-free film needs 12 ~ 14 layers.

5. Results

10

XRD of the PZT films

- Figure 1 shows an XRD pattern of a ten-layer film made by using a coating solution prepared according to Process 1 wherein each layer was dried at 200°C for 3 min and annealed at 480°C for 15 min. A strong (111) perovskite phase indicated a highly preferred orientation. The particle size (5-6nm) is believed to contribute to this.
- 15

- The effects of drying and annealing temperature and time on the formation of perovskite PZT
- 20

- Drying and firing temperature and time were found to have an impact on the formation and orientation of perovskite PZT films. Figure 2 shows the relation of (111) orientation of PZT perovskite phase of a film made from process 1 with drying temperature. It can be seen that only for a drying temperature of 200°C, were the films fully (111) oriented, at the drying temperature of about 350°C, the films had the biggest (100) orientation.
- 25

Figure 3 shows the relation of annealing temperature and time for the formation of perovskite PZT phase for a three-layer film made by method 1. Each layer was annealed at 480°C for 15 min.

5 **The effect of particle size of the solution on the formation of perovskite PZT.**

Figure 4 shows the XRD patterns of the PZT films made by using sols with different particle size. All the films had ten layers and each layer
10 was dried at 200°C and annealing at 480°C for 15 min. It was found that only when the particle size was less than 9nm could the films have a pure perovskite phase at the specified film making conditions.

15 **The effect of acetic acid amount in the solution on the formation of perovskite PZT**

Figure 5 shows the XRD patterns of three films each made from a precursor sol according to one of processes 1-3. Each film had ten layers with each layer dried at 200°C for 3 min and fired at 480°C for 10 min.
20 Pyrochlore phase was only observed in the film made by using lead acetate: Acetic acid ratio of 1g: 1ml solution. The intensity of (111) perovskite for the three films defined by ratio lead acetate to acid is 1:1 < 1:2 and 1:3; 1:2 ≈ 1:3. For the films with 1:2 and 1:3, the ratio of I_{111}/I_{100} was about 200/1, but for the film of 1:1, I_{111}/I_{100} was about
25 50/1.

The effect of firing two layers together on the formation of perovskite PZT

Films were made by the solution of Process 2. Under the coating
5 conditions of method 2, the intensity of [111] orientation was higher when firing the film at 460°C for 2 hours rather than at 480°C for 30 mins although there was no [100] orientation appearing in either film.

Fig. 6 shows the XRD patterns of two 12-layer PZT films annealed at
10 460°C and 480°C, respectively, with two layers fired together. In general, strong [111]-only orientation films can be made by the methods of either firing one layer (method 1) or two layers (method 2) at 460°C or 480°C.

15 6. Dielectric and pyroelectric properties

One layer fired

Table 1 lists the parameters for the ten-layer films made according to
20 method 1 but with different firing temperatures using the solution of Process 1. Drying was at 200°C for 3 mins. Firing was at 440°C, 460°C, 480°C or 500°C for 2h, 1h, 15 min or 5 min for each layer respectively.

25 For the measurement of electric properties, a set of Au/Cr electrode dots of 3.14 mm² was sputtered onto the film. An exposed Pt bottom electrode beneath the film provided the other electrode. A Genrad 1689M RLC Digibridge impedance analyser was used to measure dielectric properties and a Radiant Technologies RT66A ferroelectric test system was used to
30 obtain ferroelectric hysteresis loops. Pyroelectric coefficients were

obtained by measuring the pyroelectric currents generated by the specimens when under constant heating and cooling rates.

Table 1 Parameters used to calculate the merit figures of the thin films at 1KHZ (and at 33Hz in brackets).

| Firing Temp. (°C) | Pyro. Coefficient (C/Km ²) | Dielectric Cons. | Dielectric loss | Mp(P _a ^{-0.5}) |
|----------------------|--|---------------------|--------------------|---|
| 440 | 8.83 x 10 ⁻⁵ | 334(375) | 0.368(0.114) | 8.42 x 10 ⁻⁶ (1.81 x 10 ⁻⁶) |
| 460 | 1.66 x 10 ⁻⁴ | 315(340) | 0.0477(0.057) | 2.80 x 10 ⁻⁶ (5.07 x 10 ⁻⁶) |
| 480 | 1.80 x 10 ⁻⁴ | 340(358) | 0.0215(0.043) | 8.95 x 10 ⁻⁶ (6.16 x 10 ⁻⁶) |
| 500 | 2.02 x 10 ⁻⁴ | 321(338) | 0.0279(0.046) | 9.07 x 10 ⁻⁶ (6.89 x 10 ⁻⁶) |

Two layers fired together

- 10 Process 1 was used to make the solution. The film was dried at 200°C for 3 min each layer. Two layers annealed together at 460°C for 120 min. There are 12 layers in all. Film thickness is about 1 µm.

The following Table 2 and Figure 7 summarise results of dielectric constant, pyroelectric coefficient, loss tanδ and the figure of merit of the film at the frequency of 33hz.

Table 2

| Poling Voltage | Dielectric Constant | Pyro. Coeff. | Loss (%) | Fd |
|----------------|---------------------|--------------|----------|------|
| 20 | 305 | 242 | 1.32 | 1.62 |
| 18 | 301 | 238 | 1.26 | 1.42 |
| 16 | 303 | 232 | 1.41 | 1.51 |
| 12 | 300 | 232 | 1.01 | 1.79 |
| 0 | 301 | 232 | 1.2 | 1.41 |
| -3 | 295 | 233 | 1.14 | 1.71 |
| -6 | 295 | 233 | 1.15 | 1.7 |
| -9 | 298 | 233 | 1.18 | 1.67 |
| -12 | 302 | 52 | 1.6 | 0.31 |
| -15 | 304 | -59 | 1.6 | 0.35 |
| -18 | 306 | -70 | 1.55 | 0.43 |
| -20 | 306 | -83 | 1.55 | 0.51 |
| 20 | 314 | 170 | 1.68 | 1 |
| 24 | 314 | 173 | 1.68 | 1.01 |
| 26 | 313 | 174 | 1.66 | 1.03 |
| 28 | 313 | 175 | 1.7 | 1.02 |
| 30 | 312 | 180 | 1.72 | 1.05 |
| 35 | 314 | 185 | 1.97 | 1 |
| 40 | 309 | 185 | 1.69 | 1.09 |

The breakdown voltage was found to be 70 volts, or 700 KV/cm.

5

Film dc resistivity was measured. Fig. 8 shows the relationship of the resistivity with time under a constant bias voltage 20 volts of a thin film made by method 2.

The I-V and R_y -V curves for a typical film made by method 2 are shown in Fig. 9.

The processes described herein have been developed for films with the
5 composition $\text{PbZr}_{0.3}\text{Ti}_{0.7}\text{O}_3$ (referred to as PZT30/70), but it will readily be appreciated by those skilled in the art that the same principles can readily be applied to other compositions in this solid solution system.

CLAIMS

1. A process for preparing a lead zirconate titanate precursor sol
5 comprising the steps of dissolving lead acetate in acetic acid wherein the
ratio of lead acetate to acetic acid is between 1g:1ml and 1g:3ml;
dehydrating the mixture by distillation; reacting the lead acetate solution
with a mixture of zirconium n-propoxide and titanium isopropoxide
dissolved in methanol; optionally adjusting the concentration of the
10 precursor to 0.4M using methanol; and adding ethylene glycol to the
precursor in amounts sufficient to ensure the particle size in solution is
less than 9 nanometers.
2. A process according to claim 1 wherein the ratio of a lead acetate
15 to acetic acid is between 1g:2ml and 1g:3ml.
3. A process according to claim 1 or claim 2 wherein the particle size
is between 5 and 9 nanometers.
- 20 4. A process according to claim 3 wherein the particle size is between
5 and 6 nanometers.
5. A process according to any one of the preceding claims wherein the
ratio of ethylene glycol to lead is from 1:1 to 1:5 (wt%).
25
6. A process of coating a substrate with one or more layers of lead
zirconate titanate precursor according to any one of the preceding claims
such that they adopt a substantially completely perovskite orientated phase
comprising the steps of applying a layer of the precursor to the substrate,
30 drying the layer at a temperature of 100-400°C and either a) firing the

dried layer at a temperature of 400-500°C, applying further layers if required; or b) applying and drying one or more further layers before firing the dried layers at a temperature of 400-500°C to anneal them together and applying further layers if required.

5

7. A process according to claim 6 wherein 10-14 layers are applied to the substrate.

8. A process according to claim 6 or claim 7 wherein the or each layer is dried at 200°C for 3 minutes and fired at 460-480°C for a period of 5 minutes to 2 hours.

10

9. A process according to any one of claims 6 to 8 wherein the or each layer is fired or two or more layers are annealed at 480°C for 15 minutes.

15

10. A process according to any one of claims 6 to 8 wherein the or each layer is fired at 460°C for 1 hour.

11. A process according to any one of claims 6 to 8 wherein the two or more layers are annealed at 460°C for 2 hours.

20

12. A lead zirconate titanate precursor sol made according to the process of any of claims 1 to 11 having a particle size in solution of less than 9 nanometers.

25

13. A coating for a substrate comprising a thin film of a lead zirconate titanate made according to the process of any of claims 1 to 11 having a particle size in solution of less than 9 nanometers.

30

14. A coated product comprising a substrate having a coating of a thin film of a lead zirconate titanate made according to the process of any of claims 1 to 11 having a particle size in solution of less than 9 nanometers.

5 15. A coated product according to claim 14 wherein the substrate is a silicon based substrate.

16. The use of a lead zirconate titanate film coated substrate according to claim 14 or claim 15 or made by the process of claim 6 in a device for the
10 detection of electromagnetic radiation.

17. The use according to claim 16 wherein the wavelength of the radiation lies between 3 and 14 micrometers.

15 18. The use of a lead zirconate titanate film coated substrate according to claim 14 or claim 15 or made by the process of claim 6 in a piezoelectric device.

19. The use according to claim 18 wherein the device is a microphone.
20

20. The use according to claim 18 wherein the device is an accelerometer.

21. The use according to claim 18 wherein the device is a motor.
25

22. The use according to claim 18 wherein the device is an actuator.

23. The use according to claim 18 wherein the device is a resonant device for the filtering of radio frequency signals.
30

24. A process for preparing a lead zirconate titanate precursor sol substantially as described herein.
25. A process of coating a substrate with one or more layers of lead
5 zirconate titanate substantially as described herein.
26. A lead zirconate titanate precursor sol substantially as described herein.
- 10 27. A coating comprising a thin film of lead zirconate titanate substantially as described herein.
28. A lead zirconate titanate coated product substantially as described herein.
- 15 29. Use of a lead zirconate titanate coated product substantially as described herein.
- 20 30. A process for the growth of sol gel lead zirconate titanate thin films in which lead acetate is first dissolved in acetic acid in a ratio of between 1g to 1ml and 1g to 3ml, dehydrated by distillation, titanium isopropoxide and zirconium n-propoxide are reacted in dry methanol to form a white solid which is subsequently reacted with the lead acetate solution to form a transparent solution, to which ethylene glycol is added
25 so that the particle size in solution is between 5 and 9 nanometres (as measured by photon correlation spectroscopy), it being provided that the resulting solution is spun-down onto a substrate coated with titanium and platinum, the resulting layers being dried on a hot surface maintained at between 200°C and 300°C, and subsequently being annealed on a hot
30 surface at a temperature of between 400°C and 500°C to form a

perovskite phase which exhibits the pyroelectric and piezoelectric effects after poling with an applied electric field.

31. A process for preparing a lead zirconate titanate precursor sol
5 comprising the steps of:-
- a) dissolving lead acetate in acetic acid and dehydrating the resulting solution;
 - b) reacting zirconium n-propoxide and titanium isopropoxide in methanol and reacting with the product from step (a); and
 - 10 c) adding sufficient ethylene glycol to obtain a desired particle size in solution, preferably less than 9 nanometers and more preferably between 5 and 9 nanometres.
32. A process of coating a substrate with one or more layers of lead
15 zirconate titanate having a substantially completely perovskite orientated phase comprising the steps of:-
- a) applying a layer of lead zirconate titanate precursor sol according to Claim 31 to the substrate;
 - b) drying the layer at a temperature of $< 400^{\circ}\text{C}$, preferably $< 300^{\circ}\text{C}$,
20 more preferably about 200°C , and
 - c) either i) firing the dried layer at a temperature of $< 500^{\circ}\text{C}$, preferably from 400°C to 500°C , and applying further layers if required; or ii) applying and drying one or more further layers before firing the dried layers at a temperature of $< 500^{\circ}\text{C}$, preferably from 400°C to
25 500°C , to anneal them together and applying further layers if required.

33. A lead zirconate titanate thin film having a perovskite phase when made by the process described herein.

34. Any novel feature or step of any process for producing a lead zirconate titanate thin film and/or any intermediate product(s) described herein.

1/6

Fig.1.

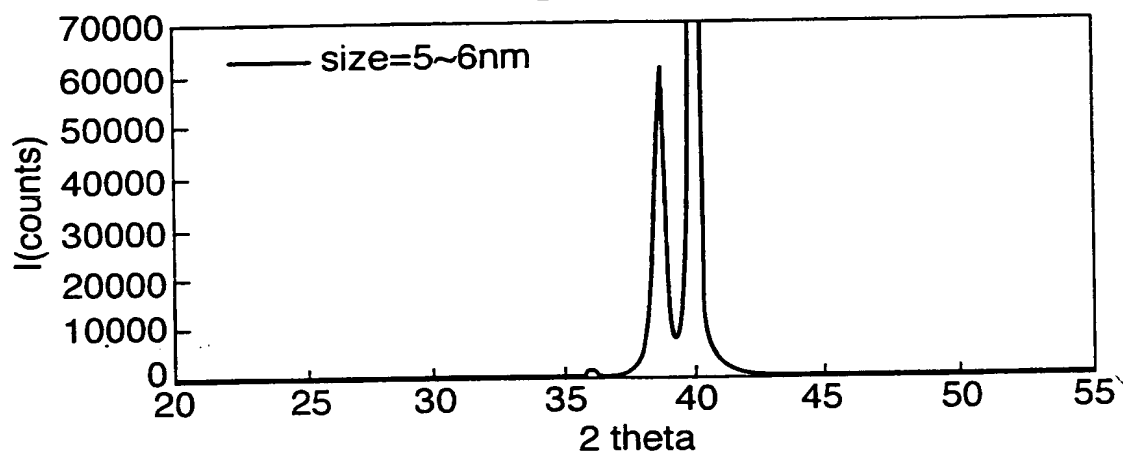
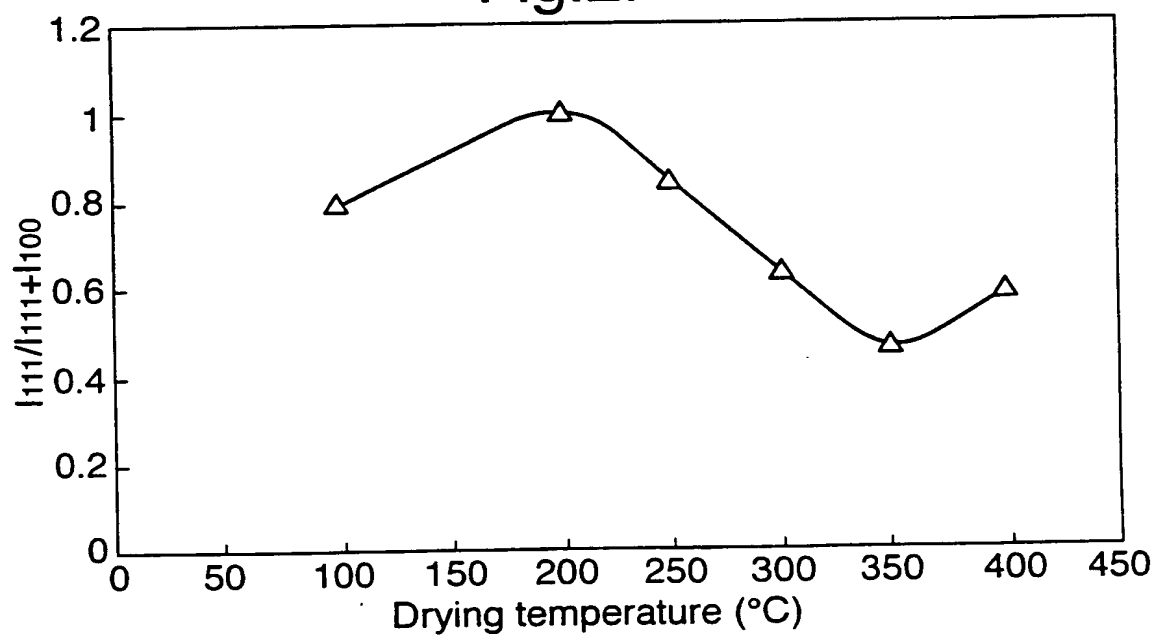


Fig.2.



SUBSTITUTE SHEET (RULE 26)

2/6

Fig.3.

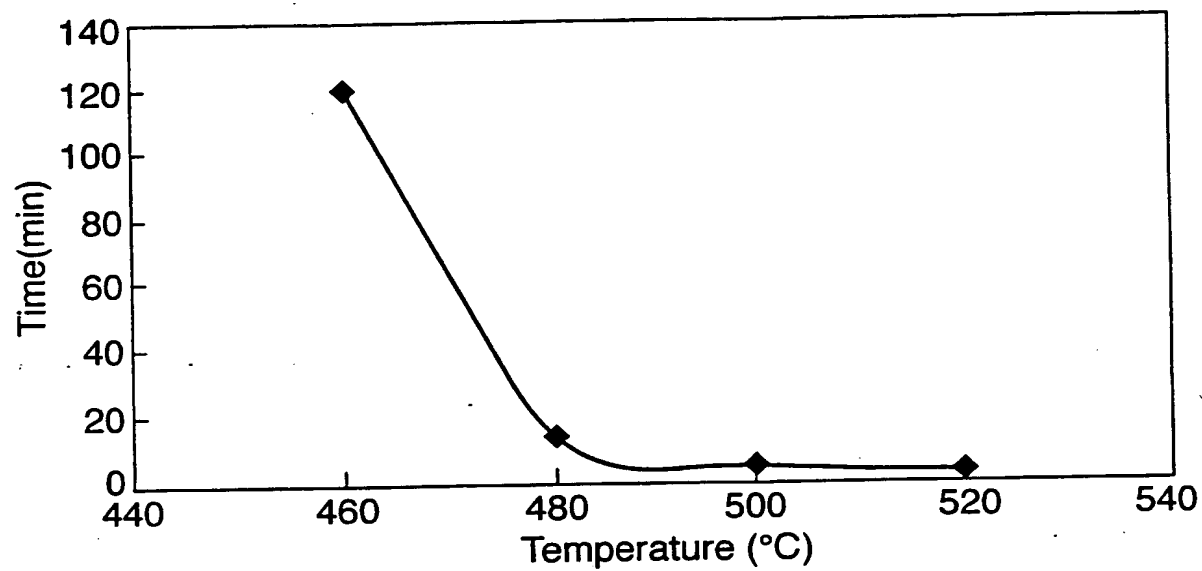
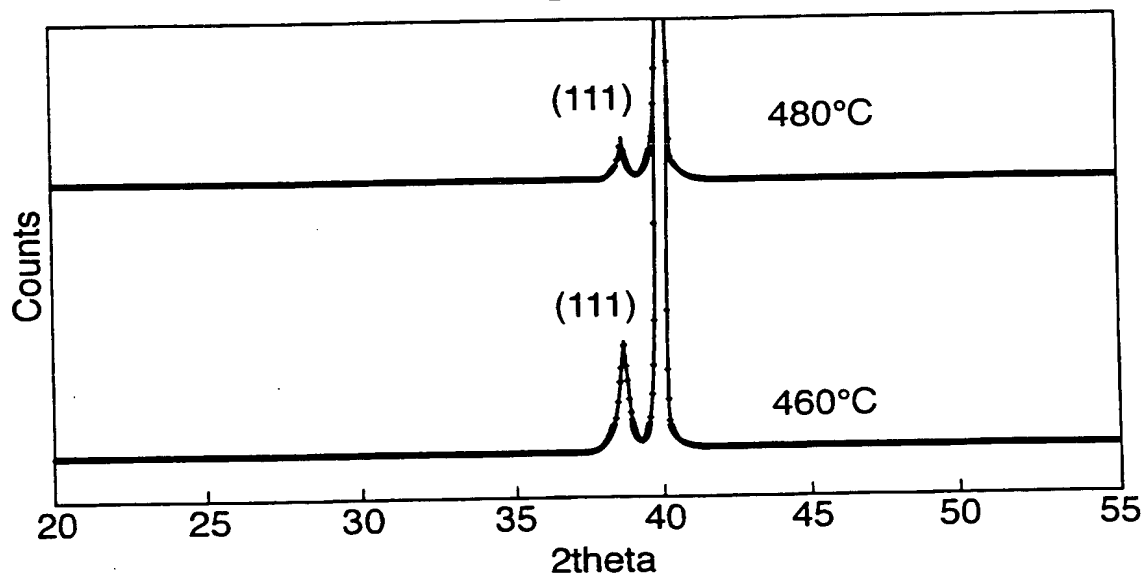


Fig.6.



SUBSTITUTE SHEET (RULE 26)

Fig.4c.

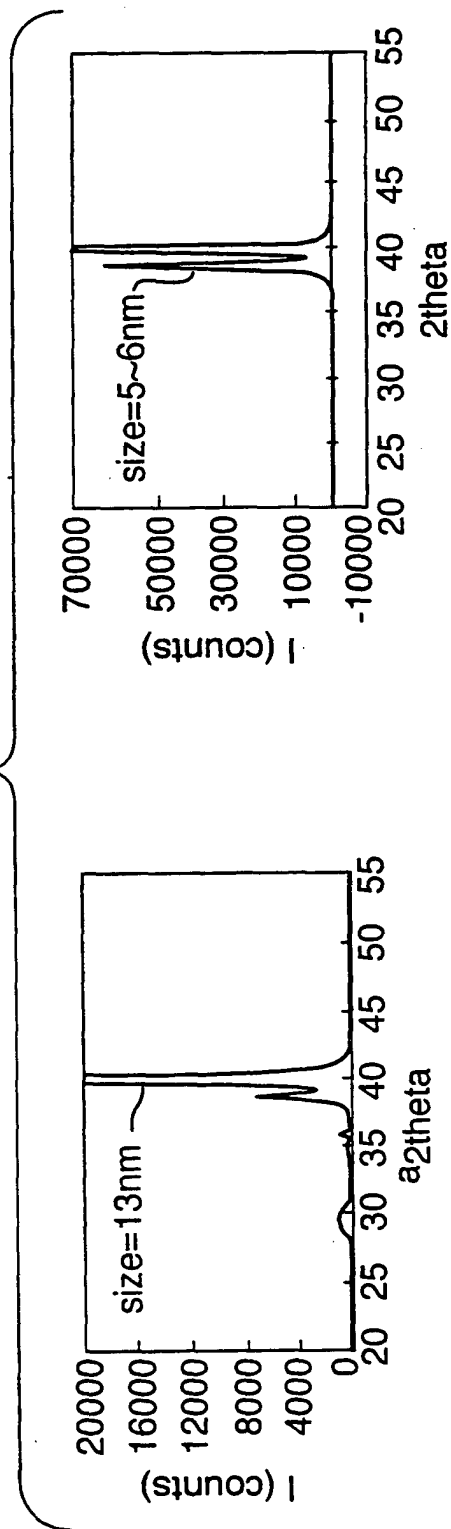
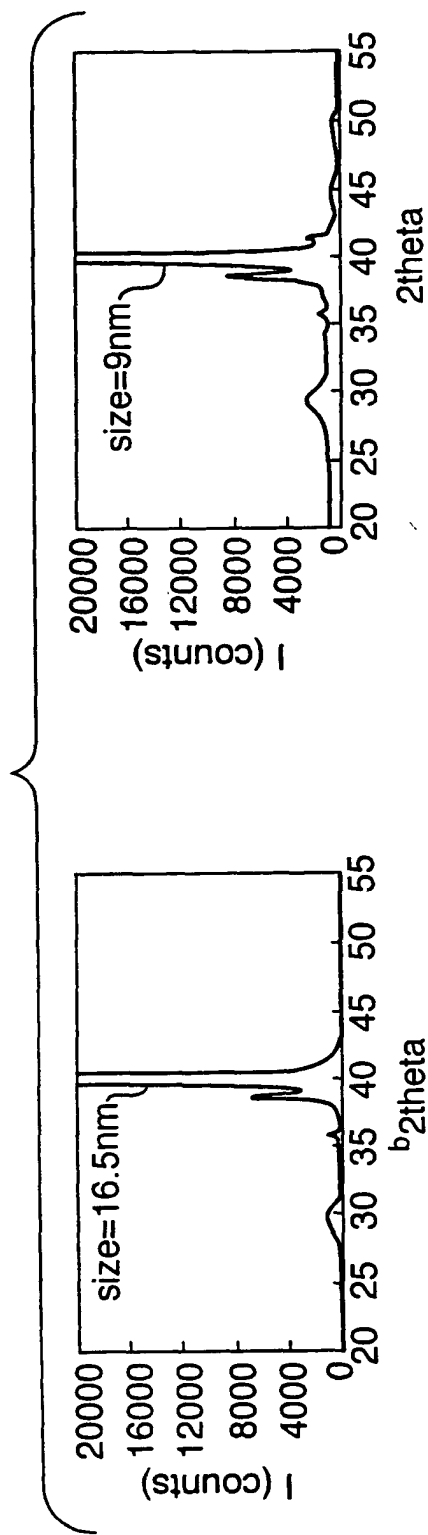
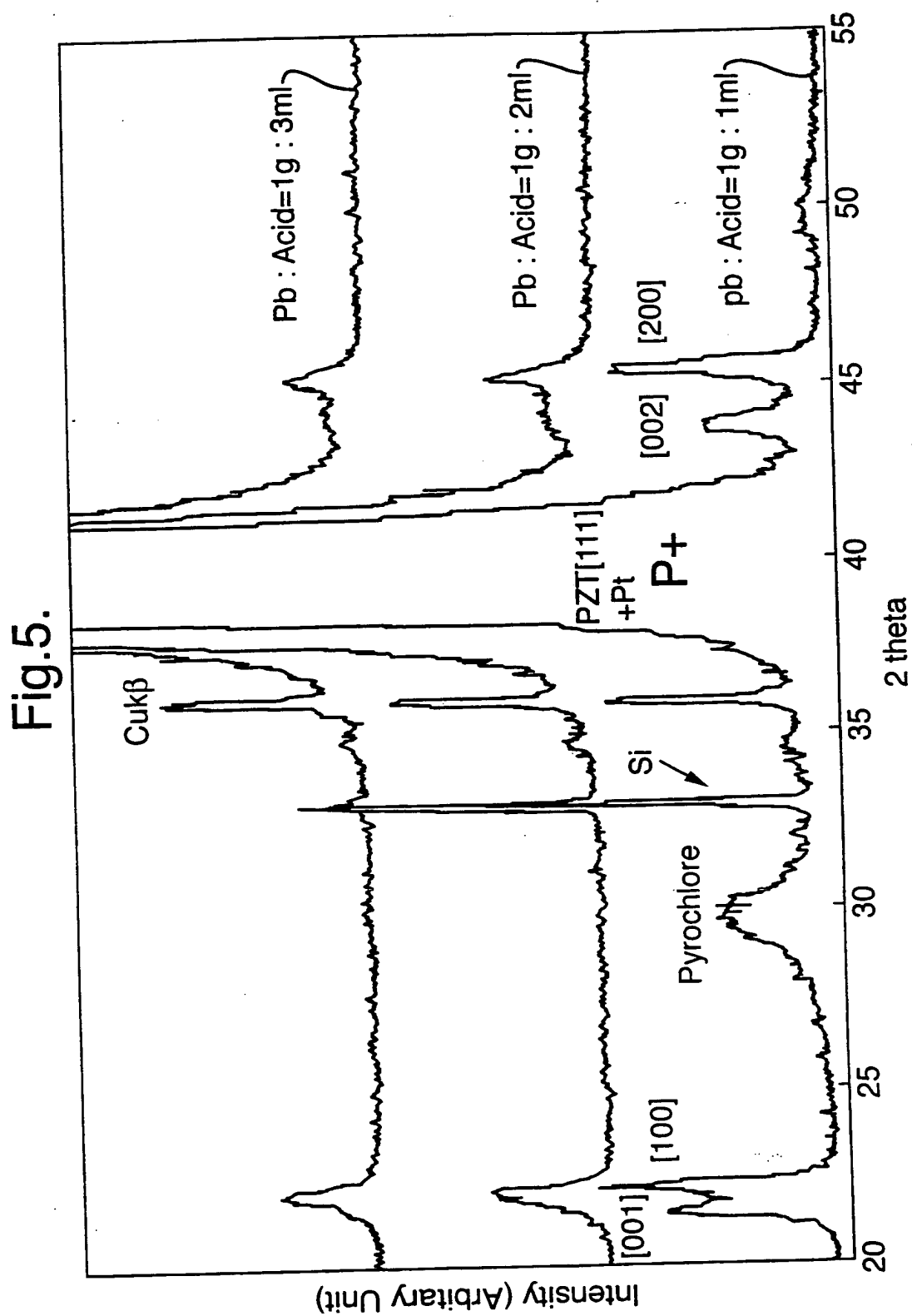


Fig.4d.



4/6



SUBSTITUTE SHEET (RULE 26)

5/6

Fig.7.

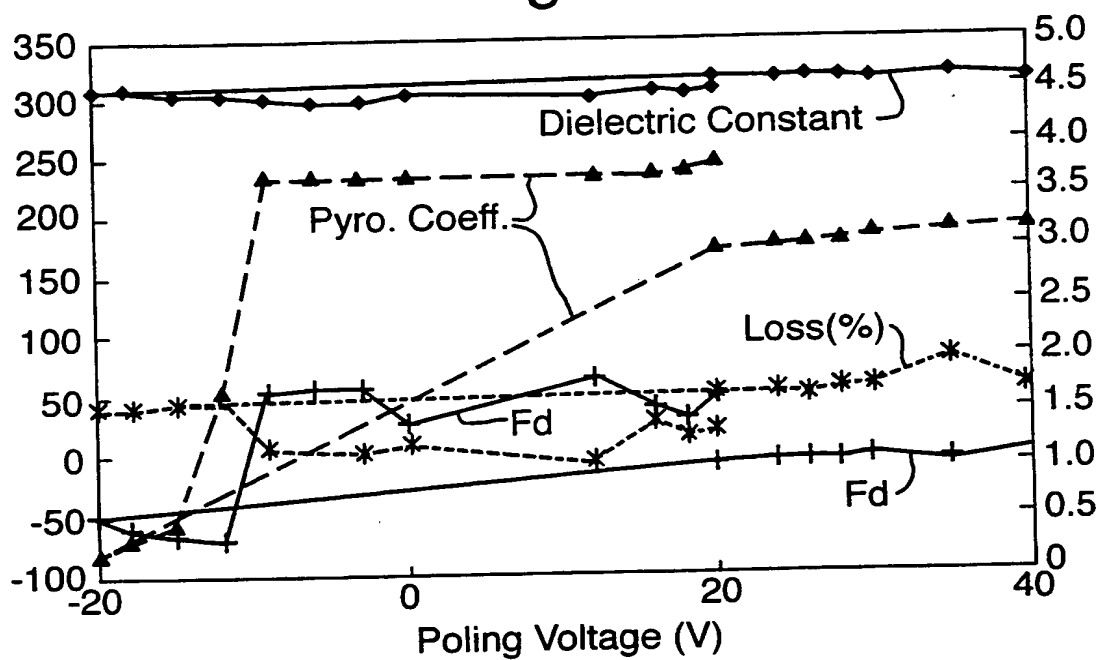
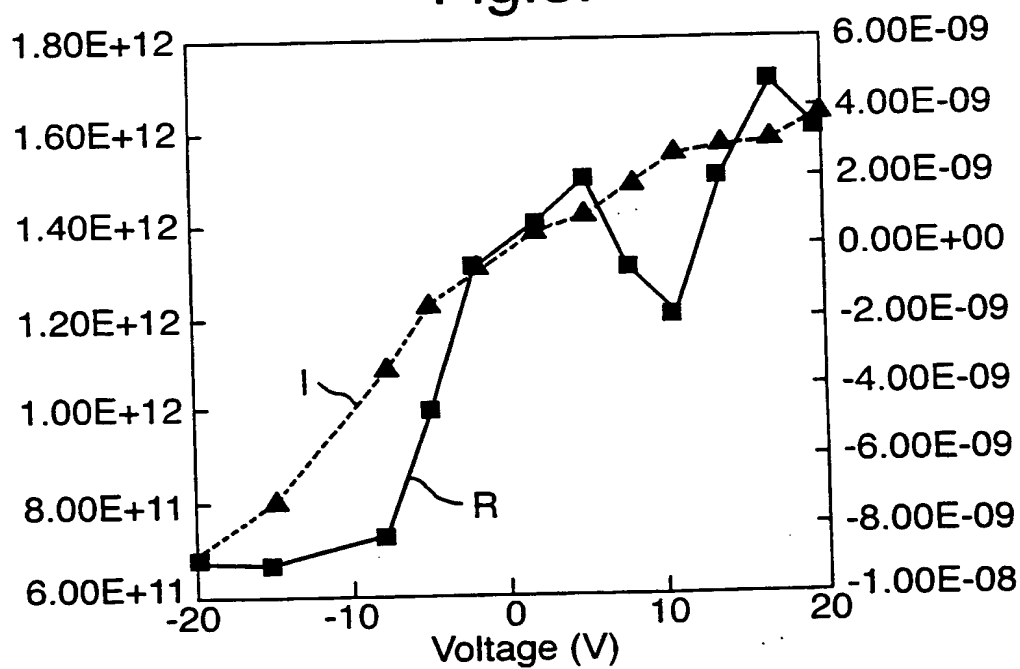


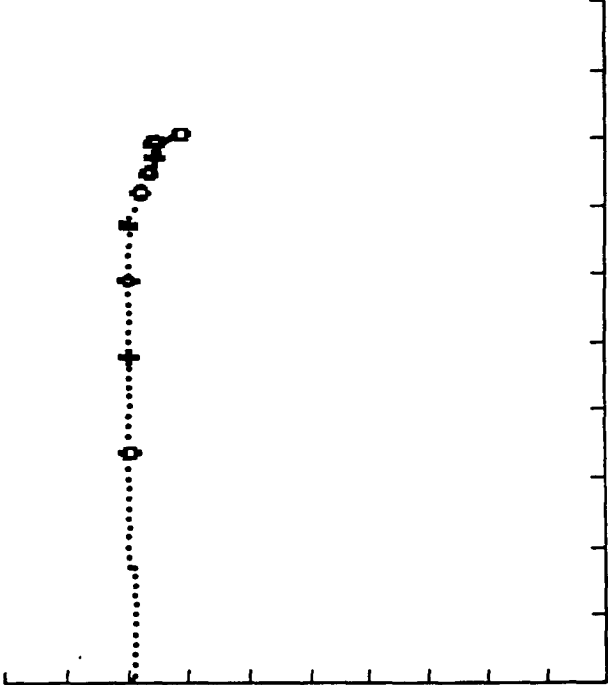
Fig.8.



SUBSTITUTE SHEET (RULE 26)

6/6

Fig.9.

| RESIST 2.2 | | RT-66A | 3/8/1999 8:55 | Profile(secs) |
|--|--|---|---------------|---------------|
| Sample: zh1no1 Log/Log(Secs) |  | X div = 4.507E-01 Y div = 1.537E+00 | Last Point | 1. 1 |
| | | | 3/8/1999 9:53 | 2. 30 |
| | | | Next Point | 3. 100 |
| | | | | 4. 300 |
| | | | | 5. 600 |
| | | | | 6. 600 |
| Ymax = 1.537E+01 Ymin = 0.000E+00 | Xmax = 4.507E+00 Xmin = -9.287E-05 | Profile #10 I = 6.5347E-08 R = 2.9371E+08 ϕRy = 9.2223E+10 | | 7. 600 |
| | | | | 8. 600 |
| | | | | 9. 600 |
| | | | | 10. 600 |
| Area(cm) = 3.14E-02 Thick(u) = 1.000 Vmax = 19.990 #Pts = 10 | | | | |
| Resistance Measurement = 249.7 ms | | | | |

SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/GB 00/01444

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 H01L21/316 C23C18/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 H01L C23C C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

INSPEC, EPO-Internal, PAJ, IBM-TDB

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|---|-------------------------------|
| X | WO 90 12755 A (ALCAN INT LTD) 1 November 1990 (1990-11-01) abstract; figure 1 | 1,2,6, 12,13, 30-34 |
| A | WO 90 13149 A (UNIV KINGSTON) 1 November 1990 (1990-11-01) abstract; figure 1 | 1,6,12, 13,16, 18,30-32 |
| | -/-- | |



Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"8" document member of the same patent family

Date of the actual completion of the international search

26 July 2000

Date of mailing of the international search report

02/08/2000

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Königstein, C

INTERNATIONAL SEARCH REPORT

Interns 31 Application No

PCT/GB 00/01444

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-----------------------|
| P,X | <p>ZHANG Q ET AL: "Effect of the particle size in PZT precursor sols on the orientation of the thin films"</p> <p>JOURNAL OF THE EUROPEAN CERAMIC SOCIETY,GB,ELSEVIER SCIENCE PUBLISHERS, BARKING, ESSEX,</p> <p>vol. 19, no. 6-7, June 1999 (1999-06), pages 1417-1421, XP004166105</p> <p>ISSN: 0955-2219</p> <p>the whole document</p> <p style="text-align: center;">----</p> | 1 |
| A | <p>YANOVSKAYA M I ET AL: "Alkoxy-derived ferroelectric PZT films: the effect of lead acetate dehydration techniques and lead content in the electrochemically prepared solutions on the properties of the films"</p> <p>INTEGRATED FERROELECTRICS, 1998, GORDON & BREACH, NETHERLANDS,</p> <p>vol. 19, no. 1-4, pages 193-209, XP000925631</p> <p>ISSN: 1058-4587</p> <p>the whole document</p> <p style="text-align: center;">-----</p> | |

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 00/01444

| Patent document cited in search report | Publication date | Patent family member(s) | Publication date |
|---|---------------------|--|--|
| WO 9012755 A | 01-11-1990 | AU 5548290 A CA 2065381 A EP 0469053 A JP 4506791 T | 16-11-1990 22-10-1990 05-02-1992 26-11-1992 |
| WO 9013149 A | 01-11-1990 | NONE | |